

The Osmotic Pressure of Cane Sugar Solutions at 15° Centigrade.

DISSERTATION

SUBMITTED TO THE BOARD OF GRADUATE STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

BRAINERD MEARS.

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EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
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INTRODUCTION.

The deviation of osmotic pressure from that of gas pressure in the vicinity of 0° centigrade while the two were found to be in close agreement near 20° has led to a series of measurements at intermediate temperatures. Results at 0°,¹ 5°,² 10°,³ and 20°,⁴ have already been obtained in this laboratory. The present investigation has been carried out at 15°.

CELLS AND MANOMETERS.

The cells designated G, D and B were employed in the measurements as they had been found to be especially trustworthy in previous work, also some new forms of cells which will be described later in this dissertation. The manometers⁵ and other apparatus were the same as those already described in connection with earlier investigations. One improvement, however, was introduced. The brass nuts employed to force the rubber stoppers on the manometers into the glass tubes of the cell and thus furnish mechanical pressure on the cell content, which had previously been fixed on the manometer tubes were slotted in such a way that they could be removed at will. This change gave a lighter instrument less subject to the danger of breaking in handling.

DEPOSITION OF MEMBRANES.

The membranes were precipitated as usual by the electrolytic method.⁶ Care was taken in depositing to keep the

¹ Am. Chem. J., 37, 425.

² *Ibid.*, 38, 175.

³ H. V. Morse, Dissertation, 1908.

⁴ Am. Chem. Jour., 36, 39.

⁵ *Ibid.*, 36, 21.

⁶ *Ibid.*, 36, 29.

temperature near 15° and thus prevent the tendency to stretch, or rupture the layer of copper ferrocyanide by the expansion or contraction of the cell wall.

PRECAUTIONS AGAINST DILUTION.

To prevent dilution of the cell contents due to the drawing in of water at the time of opening and closing, all of the cells were dipped in sugar solutions of 0.1 normal higher concentration than that in the interior of the cell, as has been previously described in this work.¹ This treatment, however while it has materially lessened the loss in rotation, did not seem to be capable of further refinement. Some advance along this line was imperative as the loss in rotation of the sugar solutions in the cell and the methods of correcting for it, whether ascribed to inversion or to one-half dilution, appeared to be the feature of the measurements most open to criticism. Believing as we did that most of this loss in rotation was caused by dilution and that it was due to subjecting the contents of the cell to diminished pressure at some stage of the measurement, we proceeded to investigate the places at which such a condition could exist. It seemed probable that very little occurred at the setting up of the cell as care was taken at that time to keep the cell contents under increased pressure while connecting the manometer and rubber stopper with the glass tube of the cell. From this point no danger could arise because of the osmotic pressure, until the operation of opening the cell at the close of the measurement. Here on withdrawing the manometer some diminished pressure was exerted as was shown by the fact that mercury was often sucked back into the cell from the bulbs of the manometer. This had been previously noted and was formerly relieved by the admission of air to the cell with a sharp pointed steel instrument pressed between the rubber stopper and the connecting-glass tube. This operation, however, did not furnish the continuous passage necessary between the interior of the cell and the atmosphere and some diminished pressure could be observed at this point. Here

¹ P. B. Dunbar, Dissertation, 1907.

then, seemed to be the place for improvement in the method. Consequently, previous to the operation of opening the cell, the stopper was pierced by a small, sharpened steel tube. A hypodermic needle about two inches long was found suitable. On penetrating the rubber stopper this tube at once afforded free communication between the interior of the cell and the external air, and, with this connection established, the manometer could be withdrawn without the least indication of diminished pressure. This procedure seemed to promise well, but we were hardly prepared for the remarkable improvement which was immediately experienced. By use of the needle no loss in rotation could be detected with the polariscope from the 0.1 through the 0.6 normal concentrations and from this point on to the normal solutions, while a loss in rotation was observed at times. It was much smaller than in any previous set of measurements. Further, this loss found in the higher concentrations tallied well with results obtained in earlier works where the polariscope was not employed, but the inversion determined by means of Fehling's solution.¹ A small change may also be accounted for by the fact that the capacity of the cell may increase slightly by the rising of the manometers and consequent dilution with water, for while, by careful manipulation, this defect has been overcome to a large extent and is absent in the lower concentrations, in the higher where the larger pressures are developed, a rise of 0.5 mm. is not unusual.

CORRECTION FOR LOSS IN ROTATION.

With this means of obtaining somewhat quantitative evidence, we can proceed to a more intelligent understanding of the causes of loss in rotation. In the first place, it is clearly shown that as a rule, little or no change in the concentration of the sugar solution takes place at the time of closing the cell. While this had been previously suspected, with no exact data at hand the best correction which could be applied to the measurements was to presuppose that an equal

¹ Am. Chem. Jour., 34, 1.

part of the dilution took place at the opening and closing of the cell, and as only the dilution which takes place during the setting up process affects the measured pressures, we were forced to determine the whole loss in rotation and subtract one-half of the result, calculated as dilution from the observed osmotic pressure. It is now obvious that this procedure was incorrect. The change in rotation observed and corrected for as one-half dilution was due to three causes: first and principally, as now known, to a dilution at the time of opening the cell which consequently did not affect the pressure as observed; second, to some inversion beginning at the 0.6 and increasing to the normal solution; and third, to a small increase in the capacity of the cell, due to the rising of the manometers and stoppers. From this evidence the conclusion follows that the previous determinations of osmotic pressure of cane-sugar up to the 0.6 normal concentrations are accurate without correction and that from this point on the results might be corrected for inversion whenever loss in rotation is observed, and we have followed this method in the present measurements.

Absolute perfection, however, has not been reached in this matter of correction for change in rotation, for while it has been proved that practically all of this loss, when the needle is employed, is due to inversion nevertheless, as is pointed out above, a trace may be due to dilution, and this at present we are unable to estimate. The quantities involved are, however, too small to essentially change the results.

Another advantage was also found in the use of the needle. It was possible to keep the manometer more completely filled with mercury as it was not sucked out at the time of opening the cell. This fact tended to prevent the sugar solution from working round between the glass and the mercury and eventually contaminating the enclosed gas. When such action occurs it is necessary to open the manometer for cleaning and refilling and to re-determine the gas volume, an operation requiring time and considerable skill.

After the closing of the cell care must be taken not to

subject its contents to mechanical pressure greater than the osmotic pressure exerted by the solution. Should such pressure be applied some water is forced out through the membrane, causing a permanent concentration of the solution under investigation as at this point the capacity of the cell is fixed; consequently, on measuring the osmotic pressure, abnormally high results are obtained and the determination is of little value. This difficulty is most often experienced in the 0.1 normal concentrations.

MATERIAL

The cane-sugar employed was the best grade of white rock candy, pulverized and dried over calcium chloride to constant weight. Two analyses gave the following results:

	I.	II.	Theoretical.
C	42.02	42.08	42.08
H	6.42	6.47	6.48

Solutions of this sugar from the 0.1 to the normal concentrations, prepared on the weight normal bases, gave identical rotations with the solutions of previous workers at the same temperatures.

The results given in Tables I to IX were obtained during the months of April and May, 1907, employing the cooling effects of hydrant water circulating through brass pipes as a temperature regulator,¹ and they were carried on until it was no longer possible to obtain 15° in the bath. We were obliged to omit the 0.1, 0.9 and normal concentrations and also several check experiments on some of the other concentrations. It was our intention to complete the series on the return of cold weather. However, in the fall several factors caused a change in the work. All of the determinations were made with manometers filled with air which has been subsequently shown to introduce the objectionable feature of shrinkage in the original air volume and to necessitate a corresponding correction of the observed pressures.² It was also difficult to decide where to begin to apply this correction to the results. Accordingly, it was determined to repeat the

¹ Am. Chem. Jour., 38, 175.

² P. B. Dunbar, Dissertation, 1907.

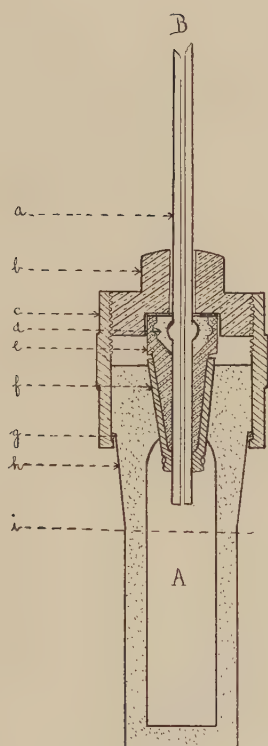
measurements with manometers filled with nitrogen, with the hope that errors from this source would be eliminated. Moreover, careful inspection of osmotic pressure data has shown that too much stress cannot be laid on the maintenance of constant temperatures, not only in the bath proper where the readings are taken, but also in the solutions and cell at the time of its closing. Variations of 0.1° change the concentration of the contents of the cell, due to sucking in or expulsion of water, and produce thermometer effects or abnormal pressures requiring three or four hours for the re-establishment of normal equilibrium conditions which seemed fatal to concordant results.

CONSTANT TEMPERATURE BATH.

To secure more accurate temperature regulation in the bath proper, the cooling device of brass pipes and flowing tap water previously described¹ was considerably improved. There appeared to be three defects in the original arrangement: first, owing to the varying pressure on the city main it was found impossible to obtain a constant flow of the cooling water through the bath; second, this water in passing through the bath, necessarily experiencing a rise in temperature, liberated some of its dissolved air which in time accumulated to form air cushions in the loops of the pipes and eventually tended to check the flow of water completely; and third, the supply of water after uniform flow was secured, varied in temperature and at some times in the year was too warm to cool the bath to the desired point.

The first of these objections was overcome by the erection of an iron standpipe of suitable length to give sufficient pressure for the circulation of the cooling water in the pipes of the bath. Hydrant water was admitted to the base of this standpipe through a valve in excess of the amount required for cooling so that, however the pressure of the supply might vary, there was sufficient water at constant pressure for the demands of the bath and a varying excess running to waste from an overflow at the top of the standpipe. The cooling water was drawn from the bottom of the standpipe

¹ Am. Chem. Jour., **38**, 175.



and an arrangement was connected to the waste pipe of the bath by which the amount of water flowing could be carefully gauged.

The formation of air cushions in the loops of the pipes was not overcome by mechanical means as it was found that by rushing water through the cooling pipes of the bath once a day, the accumulated air could be completely swept out and no serious temperature effects ensue.

The difficulty of variation in the temperature of the cooling water was overcome by employing two electric stoves, placed in tight iron cans which were submerged in the water of the bath. The stoves were incandescent electric light bulbs and were under control of a delicate mercury thermostat sensitive to 0.003 of a degree and specially designed to have all of its mercury below the surface of the water in the bath and was therefore unaffected by any fluctuation in temperature of the air above. When, however, the tap water alone was not sufficient to cool the bath to the proper temperature, previous to entering the brass pipes, it was passed through a block tin coil surrounded with ice where it was so cooled that a small flow accomplished all the lowering of temperature desired. By a suitable combination of the cooling of the circulating tap water, at times supplemented by the use of ice, and the heating effects of the regulated stoves, temperatures within 0.1° could be maintained during a measurement lasting four or five days regardless of the external conditions.

For convenience in cooling the sugar and other solutions required in setting up a cell to the proper temperatures and also to afford a place to apply mechanical pressure to the cells and watch their progress in the earlier stages of the measurement without risk of temperature changes, a smaller supplementary bath was constructed utilizing the same principles.

EXPERIMENTAL RESULTS.

There follows in Tables I. to IX. a tabulation of the results obtained in the spring of 1907. In these measurements the manometers were filled with air, the temperature regulated by the flowing tap water alone, and the hypodermic needle was not employed to prevent dilution.

Table I.

0.2 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $24^{\circ}.9$; (2) at conclusion of expr., $24^{\circ}.8$; loss, $0^{\circ}.1 = 0.40$ per cent. *Manometer*: No. 11; volume of air, 465.94; displacement, 0.01 mm. Cell used, G. Resistance of membrane, 220,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.48; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.19. Time of setting up cell, 4.00 P.M., May 7, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 7.						
11.00 P.M.	14.°8	15.°0	86.11	4.90	4.70	0.20
May 8.						
12.30 P.M.	15.°1	15.°8	85.85	4.92	4.70	0.22
4.00 P.M.	14.°8	15.°3	85.85	4.92	4.70	0.22
May 9.						
12.15 A.M.	14.°9	15.°2	86.06	4.90	4.70	0.20
				4.91	4.70	0.21

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.55.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.044.

Table II.

0.3 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $36^{\circ}.6$; (2) at conclusion of expr., $36^{\circ}.6$; loss, 0. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.28 mm. Cell used, B. Resistance of membrane, 367,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.9. Time of setting up cell, 12.30 P.M., May 11, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 11.						
8.00 P.M.	15.°1	16.°6	61.29	7.32	7.05	0.27
May 12.						
12.00 M.	15.°1	15.°1	61.43	7.30	7.05	0.25
May 13.						
9.00 A.M.	15.°0	15.°2	61.31	7.30	7.05	0.25
				7.31	7.05	0.26

Molecular osmotic pressure, 24.37.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.037.

Table III.

0.4 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $47^{\circ}.8$; (2) at conclusion of expr., $47^{\circ}.5$; loss, $0^{\circ}.3 = 0.62$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.13 mm. Cell used, G. Resistance of membrane, 223,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.01. Time of setting up cell, 4 P.M., May 13, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 13.						
11.00 P.M.	15.°1	16.°7	46.56	9.76	9.40	0.36
May 14.						
11.00 A.M.	15.°2	15.°5	46.57	9.76	9.40	0.36
5.00 P.M.	15.°0	15.°8	46.64	9.74	9.40	0.34
				9.75	9.40	0.35

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.38.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.037.

Table IV.

0.5 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $58^{\circ}.8$; (2) at conclusion of expr., $58^{\circ}.2$; loss, $0^{\circ}.6 = 1.02$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.01 mm. Cell used, D. Resistance of membrane, 367,000. *Corrections*: (1) atmospheric pressure, $\left\{ \begin{smallmatrix} 0.99 \\ 1.00 \end{smallmatrix} \right\}$; (2) liquids in manometer, 0.53; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.27. Time of setting up cell, 5.00 P.M., May 9, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 9.						
8.00 P.M.	14.°4	16.°8	37.35	12.26	11.72	0.54
May 10.						
8.30 A.M.	15.°1	16.°6	37.35	12.26	11.75	0.51
5.00 P.M.	15.°2	16.°0	37.45	12.24	11.74	0.50
				12.25	11.74	0.51

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.50.

Molecular gas pressure, 23.48.

Ratio of osmotic to gas pressure, 1.044.

Table V.

0.6 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $69^{\circ}.3$; (2) at conclusion of expr., $68^{\circ}.7$; loss, $0^{\circ}.6 = 0.87$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.09 mm. Cell used, B. Resistance of membrane, 363,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.54; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.89. Time of setting up cell, 3 P.M., May 6, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 6.						
11.00 P.M.	15.°4	16.°0	31.32	14.73	14.11	0.62
May 7.						
11.00 A.M.	15.°0	14.°9	31.37	14.71	14.09	0.62
4.30 P.M.	15.°0	16.°2	31.31	14.74	14.09	0.65
				14.73	14.10	0.63

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.55.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.045.

Table VI.

0.6 Wt. normal solution. Exp., No. 2. *Rotation*: (1) original, $69^{\circ}.3$; (2) at conclusion of expr., $68^{\circ}.8$; loss, $0^{\circ}.5 = 0.72$ per cent. *Manometer*: No. 13; volume of air, 435.09; displacement, 0.04 mm. Cell used, D. Resistance of membrane, 219,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.64; (3) dilution, 0.07; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.73. Time of setting up cell, 4.00 P.M., May 6, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 6.						
11.00 P.M.	15.°4	16.°0	28.70	14.76	14.11	0.65
May 7.						
11.00 A.M.	15.°0	14.°9	28.73	14.74	14.09	0.65
4.00 P.M.	15.°0	16.°2	28.65	14.78	14.09	0.69
				14.76	14.09	0.67

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.60.

Molecular gas pressure, 23.48.

Ratio of osmotic to gas pressure, 1.048.

Table VII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $79^{\circ}.2$; (2) at conclusion of expr., $78^{\circ}.25$; loss, $0^{\circ}.95 = 1.2$ per cent. *Manometer*: No. 13; volume of air, 435.09; displacement, 0.29 mm. Cell used, D. Resistance of membrane, 223,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.65; (3) dilution, 0.14; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.09. Time of setting up cell, 4.00 P.M., May 13, 1907.

Time.	Temperature.			Volume air.	Pressure.		
	Solution.	Manometer.			Osmotic.	Gas.	Difference.
May 13.							
11.00 P.M.	15.°1	16.°7	24.48		17.30	16.45	0.85
May 14.							
11.00 A.M.	15.°2	15.°5	24.46		17.32	16.45	0.87
5.00 P.M.	15.°0	15.°8	24.48		17.30	16.44	0.86
					17.31	16.45	0.86

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.73.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.052.

Table VIII.

0.8 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $89^{\circ}.0$; (2) at conclusion of expr., $87^{\circ}.95$; loss, $1^{\circ}.05 = 1.18$ per cent. *Manometer*: No. 13; volume of air, 435.09; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.65; (3) dilution, 0.16; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.39. Time of setting up cell, 5 P.M., April 27, 1907.

Time.	Temperature.			Volume air.	Pressure.		
	Solution.	Manometer.			Osmotic.	Gas.	Difference.
April 28.							
9.00 P.M.	15.°0	14.°0	21.44		19.81	18.79	1.02
April 29.							
8.30 A.M.	14.°7	15.°0	21.43		19.81	18.77	1.04
5.00 P.M.	14.°6	15.°25	21.43		19.81	18.77	1.04
					19.81	18.78	1.03

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.76.

Molecular gas pressure, 23.48.

Ratio of osmotic to gas pressure, 1.055.

Table IX.—Summary of Results.

Concentrations.	Temperature.	Loss in rotation.	Correction for dilution.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.2	14.9	0°.1	0.01	4.91	4.70	0.21	24.55	23.50	1.044
0.3	15.1	0°.0	0.00	7.31	7.05	0.26	24.37	23.50	1.037
0.4	15.1	0°.3	0.04	9.75	9.40	0.35	24.38	23.50	1.037
0.5	14.9	0°.6	0.09	12.25	11.74	0.51	24.50	23.48	1.044
0.6	15.1	0°.6	0.09	14.73	14.10	0.63	24.55	23.50	1.045
0.6	15.1	0°.5	0.07	14.76	14.09	0.67	24.60	23.48	1.048
0.7	15.1	0°.95	0.14	17.31	16.45	0.86	24.73	23.50	1.052
0.8	14.8	1°.05	0.16	19.81	18.78	1.03	24.76	23.48	1.055

The results in the following tables were obtained after the completion of the improvements in the temperature regulation of the bath which have already been described and also had the advantage of the use of the hypodermic needle in the opening of the cell. The manometers employed were filled with nitrogen and their gas volumes recently determined.

The results of one of the earlier measurements furnish such an excellent duplicate of a 0.3 cane-sugar solution of this series that it was introduced for the sake of comparison in the tables to follow. This procedure was justified as in the measurement in question there was no loss in rotation.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $12^{\circ}.7$; (2) at conclusion of expr., $12^{\circ}.7$; loss, 0. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.05 mm. Cell used, G. Resistance of membrane, 535,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.43; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.96. Time of setting up cell, 3.00 P.M., Apr. 9, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Apr. 11.						
3.30 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.0	143.77	2.47	2.35	0.12
Apr. 12.						
9.00 A.M.	15 $^{\circ}$.0	14 $^{\circ}$.8	143.25	2.46	2.35	0.11
				2.47	2.35	0.12

Molecular osmotic pressure, 24.65.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.049.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $12^{\circ}.7$; (2) at conclusion of expr., $12^{\circ}.7$; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.01 mm. Cell used, A₃. Resistance of membrane, 28,421. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.13. Time of setting up cell, 4.00 P.M., Apr. 28, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Apr. 29.						
10.00 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.6	158.29	(2.46)	2.35	
Apr. 30.						
8.30 A.M.	15 $^{\circ}$.0	15 $^{\circ}$.8	157.27	2.48	2.35	0.13
12.30 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.4	157.61	2.48	2.35	0.13
2.30 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.6	157.37	2.49	2.35	0.14
				2.48	2.35	0.13

Molecular osmotic pressure, 24.83.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $24^{\circ}.9$; (2) at conclusion of expr., $24^{\circ}.8$; loss, $0^{\circ}.1 = 0.4$ per cent. *Manometer*: No. 11; volume of nitrogen, 465.94; displacement, 0.01 mm. Cell used, G. Resistance of membrane, 220,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.48; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.19. Time of setting up cell, 4.00 P.M., May 7, 1907.

Time. May 7.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
11.00 P.M.	$14^{\circ}.8$	$15^{\circ}.0$	86.11	4.90	4.70	0.20
May 8.						
12.30 P.M.	$15^{\circ}.1$	$15^{\circ}.8$	85.85	4.92	4.70	0.22
4.00 P.M.	$14^{\circ}.8$	$15^{\circ}.3$	85.85	4.92	4.70	0.22
May 9.						
12.00 M.	$14^{\circ}.9$	$15^{\circ}.2$	86.06	4.90	4.70	0.20
				4.91	4.70	0.21

Molecular osmotic pressure, 24.55.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.044.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $25^{\circ}.0$; (2) at conclusion of expr., $25^{\circ}.0$; loss, 0. *Manometer*: No. 24; volume of nitrogen, 472.58; displacement, 0.06 mm. Cell used, B₃. Resistance of membrane, 377,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.26. Time of setting up cell, 12.00 M., May 3, 1908.

Time. May 4.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
8.30 A.M.	$15^{\circ}.0$	$15^{\circ}.0$	88.66	4.89	4.70	0.19
12.30 P.M.	$15^{\circ}.0$	$14^{\circ}.9$	88.63	4.89	4.70	0.19
10.00 P.M.	$15^{\circ}.0$	$15^{\circ}.0$	88.34	4.91	4.70	0.21
May 5.						
8.30 A.M.	$15^{\circ}.0$	$15^{\circ}.0$	88.64	4.89	4.70	0.19
				4.90	4.70	0.20

Molecular osmotic pressure, 24.50.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.043.

Table V.

0.3 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $36^{\circ}.6$; (2) at conclusion of expr., $36^{\circ}.6$; loss, 0. *Manometer*: No. 21; volume of nitrogen, 477.75; displacement, 0.28 mm. Cell used, B. Resistance of membrane, 367,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.9. Time of setting up cell, 12.30 P.M., May 11, 1907.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 11.						
8.00 P.M.	15°.1	16°.6	61.29	7.32	7.05	0.27
May 12.						
12.00 M.	15°.1	15°.1	61.43	7.30	7.05	0.25
May 13.						
9.00 A.M.	15°.0	15°.2	61.31	7.30	7.05	0.25
				7.31	7.05	0.26

Molecular osmotic pressure, 24.37.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.037.

Table VI.

0.3 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $36^{\circ}.7$; (2) at conclusion of expr., $36^{\circ}.7$; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.04 mm. Cell used, B₃. Resistance of membrane, 224,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.6. Time of setting up cell, 5.00 P.M., May 8, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 9.						
8.30 A.M.	15°.0	15°.0	60.97	7.37	7.05	0.32
May 10.						
1.00 A.M.	15°.0	15°.1	61.18	7.34	7.05	0.29
11.00 P.M.	15°.0	15°.2	61.10	7.34	7.05	0.29
				7.35	7.05	0.30

Molecular osmotic pressure, 24.50.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.043.

Table VII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 47.9; (2) at conclusion of expr., 47°.9; loss, 0. *Manometer*: No. 13; volume of nitrogen, 438.84; displacement, 0.02 mm. Cell used, B₃. Resistance of membrane, 560,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.17. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 17.						
12.00 M.	15°.0	15°.8	42.70	9.77	9.40	0.37
4.00 P.M.	15°.1	15°.6	42.63	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	42.70	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	42.67	9.77	9.40	0.37
				9.77	9.40	0.37

Molecular osmotic pressure, 24.43.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.039.

Table VIII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 47°.9; (2) at conclusion of expr., 47°.9; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, A₃. Resistance of membrane, 70,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 17.						
7.00 A.M.	15°.1	15°.8	46.53	9.77	9.40	0.37
12.00 M.	15°.0	15°.8	46.51	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	46.52	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	46.48	9.78	9.40	0.38
				9.78	9.40	0.38

Molecular osmotic pressure, 24.45.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $58^{\circ}.7$; (2) at conclusion of expr., $58^{\circ}.7$; loss, 0. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.51 mm. Cell used, A_3 . Resistance of membrane, 26,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.47. Time of setting up cell, 4.00 P.M., Apr. 21, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Apr. 21.						
11.00 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.3	32.06	(12.27)	11.75	(0.52)
Apr. 22.						
9.00 A.M.	15 $^{\circ}$.0	15 $^{\circ}$.1	32.03	12.29	11.75	0.54
12.00 M.	15 $^{\circ}$.0	15 $^{\circ}$.2	32.04	12.28	11.75	0.53
3.00 P.M.	15 $^{\circ}$.0	15 $^{\circ}$.4	31.99	12.30	11.75	0.55
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.046.

Table X.

0.5 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $58^{\circ}.7$; (2) at conclusion of expr., $58^{\circ}.7$; loss, 0. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, B_3 . Resistance of membrane, 122,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.19. Time of setting up cell, 4.30 P.M., May 12, 1908.

Time.	Temperature.		Volume. N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 13.						
8.30 A.M.	15 $^{\circ}$.0	16 $^{\circ}$.0	32.07	12.27	11.75	0.52
May 14.						
8.30 A.M.	15 $^{\circ}$.1	16 $^{\circ}$.1	31.99	12.30	11.75	0.55
3.00 P.M.	15 $^{\circ}$.1	16 $^{\circ}$.3	32.02	12.29	11.75	0.54
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.

Molecular gas pressure, 23.50.

Ratio of osmotic to gas pressure, 1.046.

Table XI.

0.6 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $69^{\circ}.1$; (2) at conclusion of expr., $69^{\circ}.1$; loss, 0. *Manometer*: No. 21; volume of nitrogen, 362.46; displacement, 0.18 mm. Cell used, G. Resistance of membrane, 121,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.70. Time of setting up cell, 4.30 P.M., Apr. 22, 1908.

Time.	Temperature.			Pressure.		
	Solution.	Manometer.	Volume N_2 .	Osmotic.	Gas.	Difference.
Apr. 23.						
4.30 P.M.	$15^{\circ}.0$	$15^{\circ}.6$	23.56	14.91	14.09	0.82
9.30 "	$15^{\circ}.0$	$15^{\circ}.4$	23.57	14.91	14.09	0.82
Apr. 24.						
8.30 A.M.	$15^{\circ}.0$	$15^{\circ}.4$	23.59	14.90	14.09	0.81
				14.91	14.09	0.82

Molecular osmotic pressure, 24.85.

Molecular gas pressure, 23.48.

Ratio of osmotic to gas pressure, 1.058.

Table XII.

0.6 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $69^{\circ}.1$; (2) at conclusion of expr., $69^{\circ}.1$; loss, 0. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 273,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.79. Time of setting up cell, 4.30 P.M., April 22, 1908.

Time.	Temperature.			Pressure.		
	Solution.	Manometer.	Volume N_2 .	Osmotic.	Gas.	Difference.
Apr. 23.						
4.30 P.M.	$15^{\circ}.0$	$15^{\circ}.6$	28.54	14.79	14.09	0.70
Apr. 24.						
8.30 A.M.	$15^{\circ}.0$	$15^{\circ}.4$	28.50	14.82	14.09	0.73
12.30 P.M.	$15^{\circ}.0$	$15^{\circ}.6$	28.52	14.81	14.09	0.72
				14.81	14.09	0.72

Molecular osmotic pressure, 24.68.

Molecular gas pressure, 23.48.

Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $79^{\circ}.0$; (2) at conclusion of expr., $78^{\circ}.9$; loss, $0^{\circ}.10 = 0.13$ per cent. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, A_3 . Resistance of membrane, 56,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.59. Time of setting up cell, 3.00 P.M., May 20, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 21.						
3.00 P.M.	15°.0	15°.8	22.81	17.39	16.44	0.95
11.30 "	15°.0	16°.0	22.80	17.40	16.44	0.96
May 22.						
6.00 A.M.	15°.0	15°.7	22.80	17.40	16.44	0.96
10.00 "	15°.0	15°.9	22.80	17.40	16.44	0.96
				17.40	16.44	0.96

Molecular osmotic pressure, 24.86.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $79^{\circ}.0$; (2) at conclusion of expr., $78^{\circ}.95$; loss, $0^{\circ}.05 = 0.06$ per cent. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.10 mm. Cell used, B_3 . Resistance of membrane, 293,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.46. Time of setting up cell, 3.30 P.M., May 20, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 21.						
5.00 P.M.	15°.0	16°.0	26.65	17.35	16.44	0.91
May 22.						
6.00 A.M.	15°.0	15°.7	26.64	17.35	16.44	0.91
10.00 "	15°.0	15°.9	26.66	17.34	16.44	0.90
				17.35	16.44	0.91

Molecular osmotic pressure, 24.79.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.055.

Table XV.

0.8 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $89^{\circ}.05$; (2) at conclusion of expr., $88^{\circ}.85$; loss, $0^{\circ}.2 = 0.22$ per cent. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.11 mm. Cell used, G. Resistance of membrane, 210,000. *Corrections*: (1) atmospheric pressure, 1.0; (2) liquids in manometer, 0.60; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 16.19. Time of setting up cell, 4.30 P.M., May 14, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 15.						
5.00 P.M.	$15^{\circ}.0$	$15^{\circ}.6$	21.18	20.04	18.79	1.25
May 16.						
3.30 A.M.	$15^{\circ}.0$	$15^{\circ}.4$	21.19	20.03	18.79	1.24
6.30 "	$15^{\circ}.0$	$15^{\circ}.4$	21.18	20.04	18.79	1.25
				20.04	18.79	1.25

Molecular osmotic pressure, 25.05.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $88^{\circ}.7$; (2) at conclusion of expr., $88^{\circ}.55$; loss, $0^{\circ}.15 = 0.17$ per cent. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.26 mm. Cell used, D. Resistance of membrane, 263,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.66. Time of setting up cell, 5.00 P.M., May 18, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 19.						
12.00 M.	$15^{\circ}.0$	$15^{\circ}.8$	21.14	20.09	18.79	1.30
11.00 P.M.	$15^{\circ}.0$	$15^{\circ}.8$	21.16	20.07	18.79	1.28
May 20.						
11.00 A.M.	$15^{\circ}.0$	$15^{\circ}.7$	21.12	20.11	18.79	1.32
				20.09	18.79	1.30

Molecular osmotic pressure, 25.11.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $98^{\circ}.3$; (2) at conclusion of expr., $98^{\circ}.0$; loss, $0^{\circ}.3 = 0.31$ per cent. *Manometer*: No. 15; volume of nitrogen, 419.63; displacement, 0.15 mm. Cell used, D. Resistance of membrane, 112,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.60; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.39. Time of setting up cell, 4.30 P.M., May 5, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
10.00 P.M. May 6.	15° .0	15° .0	18.00	22.90	21.14	1.76
8.30 A.M. May 8.	15° .0	15° .0	17.97	22.94	21.14	1.80
2.00 P.M.	15° .0	15° .3	17.99	22.92	21.14	1.78
				22.92	21.14	1.78

Molecular osmotic pressure, 25.47.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.084.

Table XVIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $97^{\circ}.8$; (2) at conclusion of expr., $97^{\circ}.65$; loss, $0^{\circ}.15 = 0.15$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.13 mm. Cell used, G. Resistance of membrane, 210,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.21. Time of setting up cell, 5.00 P.M., May 18, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
4.30 P.M. May 19.	15° .0	15° .8	18.64	22.87	21.14	1.73
11.00 " May 20.	15° .0	15° .8	18.60	22.92	21.14	1.78
5.00 A.M.	15° .0	15° .6	18.64	22.87	21.14	1.73
12.00 M.	15° .0	15° .7	18.61	22.91	21.14	1.77
				22.89	21.14	1.75

Molecular osmotic pressure, 25.43.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.083.

Table XIX.

1.0 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $107^{\circ}.5$; (2) at conclusion of expr., $107^{\circ}.5$; loss, 0. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.33 mm. Cell used, D. Resistance of membrane, 180,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.88. Time of setting up cell, 4.00 P.M., Apr. 30, 1908.

Time.	Temperature.			Pressure.		
	Solution.	Manometer.	Volume N ₂ .	Osmotic.	Gas.	Difference.
May 1.						
10.30 P.M.	15° 0	15° 1	16.82	25.38	23.49	1.89
May 2.						
12.30 P.M.	15° 0	15° 1	16.82	25.39	23.49	1.90
11.00 "	15° 0	14° 8	16.81	25.41	23.49	1.92
				25.39	23.49	1.90

Molecular osmotic pressure, 25.39.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.080.

Table XX.

1.0 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $107^{\circ}.5$; (2) at conclusion of expr., $107^{\circ}.2$; loss, $0^{\circ}.3 = 0.28$ per cent. *Manometer*: No. 15; volume of nitrogen, 419.63; displacement, 1.29 mm. Cell used, G. Resistance of membrane, 180,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.55. Time of setting up cell, 4.00 P.M., Apr. 3, 1908.

Time.	Temperature.			Pressure.		
	Solution.	Manometer.	Volume N ₂ .	Osmotic.	Gas.	Difference.
May 2.						
12.30 P.M.	15° 0	15° 1	16.28	25.39	23.49	1.90
5.00 "	15° 0	15° 0	16.27	25.40	23.49	1.91
11.00 "	15° 0	14° 8	16.27	25.40	23.49	1.91
				25.40	23.49	1.91

Molecular osmotic pressure, 25.40.

Molecular gas pressure, 23.49.

Ratio of osmotic to gas pressure, 1.081.

Table XXI.—*Summary of Results.*

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	15°.0	0°.00	0.00	2.47	2.35	0.12	24.65	23.50	1.049
"	15°.0	0°.00	0.00	2.48	2.35	0.13	24.83	23.50	1.056
0.2	14°.9	0°.10	0.01	4.91	4.70	0.21	24.55	23.50	1.044
"	15°.0	0°.00	0.00	4.90	4.70	0.20	24.50	23.50	1.043
0.3	15°.1	0°.00	0.00	7.31	7.05	0.26	24.37	23.50	1.037
"	15°.0	0°.00	0.00	7.35	7.05	0.30	24.50	23.50	1.043
0.4	15°.0	0°.00	0.00	9.77	9.40	0.37	24.43	23.50	1.039
"	15°.0	0°.00	0.00	9.78	9.40	0.38	24.45	23.50	1.040
0.5	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
"	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
0.6	15°.0	0°.00	0.00	14.91	14.09	0.82	24.85	23.48	1.058
"	15°.0	0°.00	0.00	14.81	14.09	0.72	24.68	23.48	1.051
0.7	15°.0	0°.10	0.02	17.40	16.44	0.96	24.86	23.49	1.058
"	15°.0	0°.05	0.01	17.35	16.44	0.91	24.79	23.49	1.055
0.8	15°.0	0°.20	0.03	20.04	18.79	1.25	25.05	23.49	1.067
"	15°.0	0°.15	0.02	20.09	18.79	1.30	25.11	23.49	1.069
0.9	15°.0	0°.30	0.05	22.92	21.14	1.78	25.47	23.49	1.084
"	15°.0	0°.15	0.02	22.89	21.14	1.75	25.43	23.49	1.083
1.0	15°.0	0°.00	0.00	25.39	23.49	1.90	25.39	23.49	1.080
"	15°.0	0°.30	0.04	25.40	23.49	1.91	25.40	23.49	1.081

Table XXII.

	Series III. Pressures. °.	Series IV. Pressures. °-5°.	Series V Pressures. 10°.	Series VI. Pressures. 15°.
Concentration.				
0.1	2.42	2.40	2.44	2.48
0.2	4.79	4.75	4.82	4.91
0.3	7.11	7.07	7.19	7.33
0.4	9.35	9.43	9.58	9.78
0.5	11.75	11.82	12.00	12.29
0.6	14.12	14.43	14.54	14.86
0.7	16.68	16.79	17.09	17.39
0.8	19.15	19.31	19.75	20.09
0.9	21.89	22.15	22.28	22.94
1.0	24.45	24.53	25.06	25.42
Total pressures	131.71	132.68	134.75	137.49
Difference		0.97	2.07	2.74
Molecular osmotic pressure	23.95	24.12	24.50	24.98
Difference		0.17	0.38	0.48
Molecular gas pressures	22.29	22.65	23.09	23.50
Difference		0.36	0.44	0.41
Mean loss in rotation (per cent)	1.73	1.45	0.22	0.10
Mean ratio of osmotic to gas pressure	1.074	1.065	1.061	1.064

CONCLUSION.

In comparing the results (Tables I. to IX.), in which the temperature was controlled by the running tap water alone, we note variations in temperature which seem large when contrasted with those of subsequent measurements. The average temperature of the bath was, however, $15^{\circ}.1$ and in spite of these changes the series is fairly satisfactory for the conditions under which we were then working. The mean loss in rotation was 0.75%. Tables I.-VIII. give a record of the individual experiments and Table IX. a summary of the results.

The second series of results (Tables I. to XX., Series 2) were obtained under more favorable circumstances. There is practically no variation in temperature and the loss in rotation (Table XXI.) is so small as to have little influence on the measurements. A minimum point is observed as previously noted in the ratio of the osmotic to the gas pressures at the 0.4 normal concentration. This may be due to the fact that the 0.1, 0.2 and 0.3 normal concentrations are too low as our experimental errors are more evident in these concentrations—or possibly to some other influences whose action is at present obscure. A comparison is furnished between results obtained with manometers filled with air and those containing nitrogen, and the conclusion is that manometers filled with air, provided the gas volume has been recently determined, give results differing but little from those in which nitrogen is employed, and, therefore, that the previous series of measurements were not appreciably influenced by this source of error.

Table XXII. presents some interesting data. In it are given the actual pressures observed, uncorrected for loss in rotation, in the measurements at 0° , 5° , 10° , and 15° , the totals of these pressures and the differences between them, followed by the molecular osmotic pressures (the molecular osmotic pressure is obtained by dividing the sum of the pressure observed by 5.5, the sum of the concentrations of the solutions) and their differences. Also the molecular gas pressures and differences and the mean percentage loss in rota-

tion. A comparison of the differences between the molecular osmotic pressures and the corresponding differences of the molecular gas pressures brings out an interesting relationship, leaving out the values of 0.17 and 0.36 between 0° and 4° to 5° for the reason that osmotic pressure does not seem to behave normally in the vicinity of maximum density of the solvent, and also because in these series the method of measurement was less refined than in Series V. and VI. It is seen that the difference of 0.38 for the increase in molecular osmotic pressure varies but 0.06 from the corresponding difference of the molecular gas pressures between 4° to 5° and 10° and that there is even more striking agreement in these differences between 10° and 15° . Osmotic pressure then seems to increase with about the same rapidity as gas pressure between these points; but while these differences offer a basis for speculation regarding the temperature coefficient of osmotic pressure, we do not feel justified in venturing any statement as to the laws governing the same but have determined with the improved method, with its limited sources of errors, which is now available to investigate the conditions at higher temperatures and also to redetermine the pressures already obtained which are subject to any doubt because of a higher percentage of error at that time, with the hope of discovering if possible the fundamental principles governing the rise in osmotic pressure with increase in temperature.

The Development of a New Cell for the Measurement of Osmotic Pressure.

Two great obstacles have barred the way to a more rapid progress in the measurement of osmotic pressure in this laboratory. First, but less important, a sufficient supply of accurately calibrated manometers and second, the lack of a large number of cells capable of giving trustworthy measurements. By constant application the number of manometers has been increased and this want somewhat lessened, but the lack of suitable cells is still a serious problem and has continued to hinder the work up to the present time; accordingly it was decided to give this subject especial attention.

The cell now in use presents several opportunities for improvement (for a description see *Am. Chem. Jour.*, 34, 4). In the first place, it is a difficult matter to prepare one for the deposition of the membrane by setting the glass tube and soapstone washer with shellac and litharge cement and coating the exposed surfaces with rubber solution to furnish a tight joint. If this connection has the slightest leak, no matter with what care the subsequent depositing of the membrane is carried out, the cell, although of suitable texture for measurements, can never develop maximum pressure, and considerable time is lost in determining this fact. Then, too, if the joint is of excellent character, in time cracks may develop in the protecting rubber coating, thus allowing the sugar solution to corrode the litharge cement which necessitates a complete renovation and reassembling of the parts of the cell.

Another cause of trouble in the present cell is that the glass tube is subject to somewhat rough treatment at the time of closing and opening the cell, and, in spite of most

careful precautions, is scratched or weakened and subsequently cracks. Some of our most useful cells have unfortunately experienced such accidents which is a serious matter as the cell, in the process of digging out the cements and removing the membrane, is subject to injury and, without accidents, it is at least a month's time before it is in condition for use.

It was also hoped to make some improvement in the method of connecting the manometer with the cell, the process at present being time-consuming and difficult, and one subjecting the manometers to considerable danger of breaking. By reducing the time of closing which often extends over a period of twenty minutes, the danger of dilution at this point would be avoided. Then, too, after the cell has been closed by the present method the rubber stopper continues to give and requires considerable compression to make a rigid joint and often allows a slight rise of the manometers in the higher concentrations.

After a consideration of these facts it seemed necessary to abandon the glass connecting tube as it appeared to be the cause of much of the difficulty and to construct a cell which could be connected with the manometer directly. On attacking the problem with this end in view the first difficulty encountered was the impossibility of making a tight connection between the membrane of the cell and the rubber stoppers on the manometers. This is overcome in the present cell by allowing the membrane to form a connection with the permanent rubber coating on the inside of the cell which, as it is never disturbed, is quite satisfactory. It became evident that some such arrangement must still be employed, but that the rubber coating lacking the durability required was unsuitable for the purpose. It was decided to glaze that part of the cell which comes in contact with the manometer and allow this glaze to extend into the cell where the membrane could form a connection with it much the same as in the present form. The problem then was to obtain a suitable glaze, and the usual difficulties were experienced, most of the glazes obtainable showing a tendency to craze. By a careful study of the problem and numerous experiments, a

glaze with the proper coefficient of expansion was obtained and has proved quite satisfactory.

The next question was to devise a means of connecting the manometer with the cell which should not only be rapid in execution, but also furnish a joint capable of withstanding great pressures without leaking, and allow for the application of the required mechanical pressure on the enclosed sugar solutions. Several forms were planned and constructed, each of which in turn proved unsatisfactory but furnished additional knowledge of the necessary requirements which at length seems to have led to success. The familiar principle of the taper joint combined with a rubber packing is employed and a diagram of the most successful form is shown in the accompanying cut.

DESCRIPTION OF THE CELL.

The cell A is composed of the same material as those in use at present and is glazed from the top down to the line shown at *i*, both inside and out. From this line on, the wall remains porous and is suitable for the deposition of the membrane. The neck of the cell is constricted and tapers slightly from the outside to the interior. B represents a portion of the manometer which passes through the nut at *b* and enters the conical brass plug shown at *e* which is turned to the same taper as the neck of the cell and bored-out at the top for reception of a setting of Wood's metal shown at *d* which holds the manometer rigidly in place. This joint is made more secure by an enlargement of the manometer tube and a depression cut in the interior of the brass plug which will be easily understood by a glance at the diagram. The use of Wood's metal as a setting material, after unsuccessful experimentation with various sealing waxes and cements, has given excellent results. It melts easily, thus removing danger of cracking the manometers, sets quickly and rigidly and expands on cooling—three very desirable features. The rubber packing designated by *f* is slipped on the conical plug and tied securely to the manometer at its lower end with "waxedend." This rubber, if of proper quality and thickness,

should furnish a tight joint with the cell and prevent the sugar solution from coming in contact with the brass plug. The question of obtaining a suitable texture of rubber for this joint has been a troublesome one and has not as yet been settled to our satisfaction. The rubber must be soft and yielding and at the same time tough enough to withstand a tearing strain and the withdrawal of the needle without rupture or cutting. The brass nut shown at *b* is slotted in such a way that it can easily be slipped on to the manometer. A part of its lower portion is cut out to receive the top of the conical brass plug and tends to hold it in position. This nut is threaded into the brass collar at *c* which in turn grips the cell at *g* where a lead washer is employed to prevent injury to the outside of the cell.

The act of closing is carried out as follows: After filling the cell with sugar solution, the manometer, properly fitted with the brass plug and rubber washer, is forced into the neck of the cell along with a hypodermic needle which connects the interior of the cell with the air, passing between the rubber packing and the cell wall and out through the slot in the nut. The collar is slipped on the cell from below, and the nut placed on the top of the brass plug is turned on the threads of the collar till the proper pressure is exerted on the rubber packing, the needle meanwhile allowing the excess of sugar solution caused by the advance of the manometer into the cell to escape. The needle is withdrawn and as there is now no communication of the interior of the cell with the air, on turning the nut any desired pressure can be obtained and the rubber packing made more effective.

The opening is even a more simple process. The nut is unscrewed, the rubber packing pierced with the hypodermic needle and the manometer quickly withdrawn.

It is evident that this cell has some advantages over the present form. It is simple in construction and is ready for the removal of air and the deposition of the membrane after the firing of the glaze. This permits a more rapid weeding out of poor cells. The size of the membrane can easily be regulated as the interior of the cell can be glazed to any

desired point, and if too small a portion seems to have been reserved, some of the glaze can be easily removed with a carborundum wheel and the porous area increased.

The cell can be quickly closed and opened requiring about two minutes for the closing and a minute for the opening, while the present cell requires about fifteen and three minutes respectively. In the operation of opening and closing no diminished pressure is exerted and therefore no dilution arises from this cause. It is also impossible for the manometer to rise because of its rigid setting. There are no glass tubes to break, no rubber coating to disintegrate and no cements subject to corrosion.

A number of quantitative measurements have been satisfactorily completed with this cell and some of the results are given in the tables above. It is our hope that on continued use it will satisfactorily perform the function it was designed to fulfil and be of great service in the subsequent measuring of osmotic pressure.

BIOGRAPHICAL.

Brainerd Mears was born at Amherst, Massachusetts, January 17, 1881. His early training was received at Drury Academy, North Adams, Mass. He entered Williams College in September, 1899, and graduated from that institution with the B. A. degree in 1903 and with the M. A. degree in 1905. He was assistant in chemistry in Williams College for three years after graduation. In October, 1906, he entered the Johns Hopkins University as a graduate student in chemistry, his subordinate subjects being physical chemistry and geology.

